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Nanoporous metals - combining strength and porosity

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Recent nanomechanical tests on submicron metal columns[1-6] and wires[7] have revealed a dramatic increase in yield strength with decreasing sample size. This effect seems to be related to the increased strength observed in metals on decreasing grain size[8] or film thickness,[9] and has been explained by a dislocation nucleation/activation controlled plasticity regime in small sample volumes. The question arises whether one can utilize this new size effect to design materials with improved bulk properties. Here, we demonstrate that nanoporous metal foams can be envisioned as a three-dimensional network of ultrahigh-strength nano-columns/wires, thus bringing together two seemingly conflicting properties: high strength *and* high porosity. Specifically, we studied the mechanical properties of nanoporous (np) Au using a combination of nanoindentation and column microcompression tests, as well as supplemental molecular dynamics simulations. We find that np-Au can be as strong as bulk Au, despite being a highly porous material, and that the ligaments in np-Au approach the theoretical yield strength of Au. The combination of high yield strength and high porosity can be used to design a new generation of energy absorbing materials for various engineering applications.

According to current models, the mechanical properties of foams can be described by scaling equations with the relative density of the material as the dominating parameter.[10] The mechanical properties of the foam ligaments (or struts), such as the yield strength, are assumed to be bulk-like and size-independent, implying that the strength of foam materials always decreases with increasing porosity. On the other hand, recent nanomechanical measurements on submicron Au columns[1-6] and nano-wires[7], which closely resemble the ligaments in foams, have revealed a dramatic increase in strength with decreasing sample size. This leads to the question of whether the current models describing the mechanical properties of metal foams can be applied to foams with cell dimensions on the nanoscale. Our previous research on the mechanical properties of nanoporous Au reveals the need to incorporate the size effect into current foam models since the experimental yield strength was ~ 10 times higher than predicted.[11,12] However, the data did not allow us to identify the origin of the experimentally observed high yield strength.

Here, we report on a comprehensive study of the mechanical behavior of nanoporous Au as a function of ligament dimensions. Nanoporous Au exhibits a characteristic sponge-like open-cell foam structure (Fig. 1) which makes it an ideal candidate for such a case study for several reasons. First and foremost, the ligament size is (1) very uniform and (2) can be tuned from 10 nm to 1 micron without changing the relative density or relative geometry (connectivity, ligament shape, pore shape) of the material.[13-15] Second, monolithic millimeter-sized samples can easily be obtained by dealloying Ag-Au. Third, Au does not form an oxide layer. Furthermore, np-Au has recently attracted considerable interest fueled by its potential use in actuator,[16,17] sensor,[18,19] and catalyst[20] applications. Despite these exciting prospects, the understanding of the mechanical behavior of metal foams at the nanoscale is still very much in its infancy.[11,15,21]

The current study demonstrates that the ligament size has a very strong effect on the yield strength of np-Au. The mechanical properties of np-Au were tested by conventional load-controlled nanoindentation using a Berkovich tip with a radius of curvature of ~ 200 nm (Fig. 2). Note that the experiments do not test the mechanical properties of individual ligaments, but sense the mechanical response of an ensemble of ligaments and pores. Furthermore, the appearance of residual impressions reveals that plastic deformation is predominately confined to the area under the indenter since the adjacent areas are virtually undisturbed (Fig. 2b).

Figure 2a shows three sets of nanoindentation load-displacement (P-h) curves obtained from three different np-Au samples, all with a relative density of 25%, but different ligament dimensions (10, 25, and 50 nm). The overlapping loading sections of each data set demonstrate the excellent reproducibility of the measurement. More importantly, the shift of the P-h curves towards lower displacement values with decreasing ligament diameter indicates that the strength of np-Au increases with decreasing ligament diameter. This result is in contradiction to the vast body of data on macrocellular foams which unequivocally show that the strength is a function of the relative density and, to some extent, of the cell geometry, but *not* of the cell size.[10]

Standard analysis of the *P-h* data shown in Fig. 2a reveals that the indentation hardness (or contact pressure), and thus the yield strength,[22] increases from ~33 to ~171 MPa as the ligament diameter decreases from 50 nm to 10 nm. Moreover, despite being a highly porous material, np-Au with 10 nm ligaments is about as strong as bulk Au for which we measured a yield strength of ~ 150 MPa,[23] which is consistent with literature values (the yield strength of bulk Au depends strongly on the sample history, and can vary between 2-200 MPa[24,25]).

According to the standard model of foam plasticity developed by Gibson and Ashby, the relationship between yield strength (σ) and the relative density (ρ^* /ρ_s) of a foam material is given by:

$$\sigma^* = 0.3\ \sigma_s\ (\rho^* /\rho_s)^{3/2} \tag{1}$$

where * and s denote foam and bulk properties, respectively.[10] It is important to notice that the model contains no explicit length scale dependence, and assumes that the material properties of the ligaments such as the yield strength (σ_s) are size-independent and equal to the bulk value. However, recent nano-mechanical tests have revealed a strong sample size effect at the sub-micron length scale.[1-7] If we assume that the scaling equation can be applied to nanoporous metal foams, then the yield strength should be considered as a variable in order to incorporate the size effect. This allows us to use Eq. (1) to back-calculate the yield strength of Au ligaments (σ_s) from the load-displacement data shown in Fig. 2a. This interpretation of the data reveals that the yield strength of nanometer-sized ligaments increases from ~880 MPa to 4.6 GPa as the ligament diameter decreases from 50 to 10 nm (Fig 2c). Remarkably, the yield strength of the smallest ligaments reaches the theoretical shear stress $G/2\pi$ for Au (4.3 GPa).[26]

The high yield strength of the ligaments of np-Au is consistent with recent uniaxial compression tests on submicron-sized Au columns,[4-6] which have shown the general trend that "smaller is stronger". Specifically, the yield strength data of 10-50 nm ligaments are in excellent agreement with an extrapolation of the size dependence reported by Volkert and Lilleodden,[6] who observed that the yield strength of submicron Au columns follows the power low d^{-n}, where d is the column diameter and n is 0.6 (Fig. 2c). Thus, the constant σ_s in Eq.1 should be replaced by a function $\sigma_s(d)$ which depends on the ligament diameter. Several important results emerge from this discussion. First, nanoindentation is a simple and straight-forward method to measure the yield strength of nanoporous materials. Second, the yield strength of the ligaments in np-Au increases with decreasing ligament dimensions, which is consistent with the sample size effect previously reported for submicron Au columns and wires.[1-7] Third, the scaling equations can be applied to nanoporous metal foams as long as the size-scale effect on plasticity is accounted for properly. Furthermore, using np-Au as a sample considerably extends the accessible range of ligament/column dimensions for mechanical tests as the smallest diameter accessible by the FIB micromachining technique is about 100 nm.

To further validate our test method and the interpretation of the results, we performed uniaxial compression tests on micron-sized nanoporous Au columns[12] using the methodology developed by Uchic et al..[1] Briefly, freestanding micron-sized columns with an aspect ratio (height-to-diameter) of ~ 2 were machined into the surface of np-Au (Fig. 3a), and mechanically tested using a MTS nanoindenter equipped with a flat punch. These micro-compression tests confirm the very high yield strength values revealed by conventional nanoindentation. Figure 3b shows a typical stress-strain curve obtained from np-Au with a relative density of 0.3 and a ligament diameter of 40 nm. The stress-strain curve shows a linear-elastic regime followed by a plateau indicating plastic collapse. The elastic-plastic transition is observed around 90 MPa at 2.5% strain, which is consistent with the nanoindentation experiments shown in Fig. 2 once the data are corrected for the difference in relative density (see Fig. 2c). The long plateau of the stress-strain curve reveals that the high stress levels observed in the nanoindentation experiments (Fig. 2) cannot be explained by densification, at least not at strain levels below 15 %. Most importantly, it should be emphasized that the mechanical behavior of np-Au columns is controlled by the ligament size as an internal length scale[12] rather than by the physical dimensions of the columns as observed for fully dense single crystalline materials.[1-6]

To extend our study beyond the length scale accessible by experiments, we performed molecular dynamics (MD) simulations of gold columns/ligaments using the embedded atom method[27] (EAM). Here, we extend previous MD simulations on the mechanical behavior of Au nanowires[28-30] to length scales overlapping with our experimental range (10-50 nm). In short, our MD simulations confirm the high yield strength of nanometer-sized Au ligaments, but fail to reproduce the experimentally observed size dependence (smaller is stronger). Instead, we observe that the strength of defect-free, single crystalline Au columns should increase with increasing diameter. The MD result can be qualitatively understood in terms of the 1/diameter dependence of the surface-stress-induced compressive stress reported previously.[30] This leads to the important conclusion that the experimentally observed size dependence (smaller is stronger) seems to be linked by the presence of defects along the following line: the larger the ligament, the larger the defect which can be accommodated, and the lower the stress required to initiate yield. Indeed, preliminary simulations reveal that stable defects can only be accommodated by sufficiently large ligaments (at least 20 nm in diameter). Ligaments smaller than this critical size should be essentially defect-free, and the strength should therefore be controlled by the surface-to-volume ratio (smaller is weaker). In the context of np Au, this line of argument suggests that decreasing the feature size beyond 10 nm should weaken the material instead of further increasing its strength, similar to the reverse Hall-Petch regime predicted for nanocrystalline materials.

In conclusion, we have demonstrated that the recently discovered sample-size effect in plasticity can be utilized to improve the strength of metal foams by reducing the length scale of ligaments and pores. The ultimate strength in nanoporous metals can be reached when the ligaments attain the theoretical strength or, according to MD simulations, by reducing the ligament diameter to the 10 nm range. Furthermore, we have shown that the scaling equations, originally developed for macroscopic foams, can be applied to nanoporous metals by incorporating the sample-size effect.

Methods:

Disk-shaped samples of np-Au (diameter ~ 5 mm, thickness ~ 300 μm) with relative densities of 0.25 and 0.3 were prepared by selective dissolution (dealloying) of $Ag_{0.75}Au_{0.25}$ and $Ag_{0.7}Au_{0.3}$ alloys, respectively. This corrosion process generates a characteristic nanoporous sponge-like open-cell foam structure of almost pure Au.[31,32] Details of alloy preparation and dealloying procedures can be found in the literature.[11] In short, np-Au with 25 and 50 nm ligaments were prepared by free corrosion, i.e. emersion in concentrated nitric acid (70%), and the pore size was adjusted by the immersion time (typically between 2 and 5 days). The np-Au sample with 10 nm ligaments was prepared by electrochemically-driven dealloying, i.e. by applying a potential of ~ 1V measured versus a Ag pseudo-reference electrode in a 1 M HNO_3 + 0.01 M $AgNO_3$ electrolyte. The complete removal of Ag was verified by energy dispersive X-ray spectroscopy, and pore/ligament size was measured by scanning electron microscopy (SEM).

The mechanical properties of nanoporous Au were tested by depth-sensing nanoindentation using a Triboindenter (Hysitron) equipped with a diamond Berkovich indenter tip (radius of ~ 200 nm). Indentations were performed on polished surfaces (polished before dealloying) using a constant loading rate of 500 μN/s with loads ranging from 200 to 1800 μN. Columns of np-Au for linear compression tests were prepared in the surface of the samples by focused ion beam (FIB) microfabrication techniques. They were compressed using a flat diamond punch in a nanoindenter (MTS NanoXP) at a constant loading rate of 25 μN/s, and then unloaded following a 15 s hold. Details of both fabrication and testing can be found elsewhere.[6,12]

The MD simulations were performed using the EAM potential by Foiles, et al..[27] All simulations were performed on [001]-oriented cylindrical systems with cubic symmetry and free boundary conditions in all three directions. The dimensions of the Au columns ranged from 4nm x 8nm (containing 7300 atoms) to 50 nm x 100 nm (containing 14,267,250 atoms) in diameter and length, respectively. All systems were initially equilibrated to zero pressure at 50K for several picoseconds. After the relaxation, we proceeded to compress the columns uniaxially along the z-direction (001 orientation) at strain rates from 2×10^7 s^{-1} to 1×10^9 s^{-1}, and measured the stress vs. strain response.

Acknowledgements

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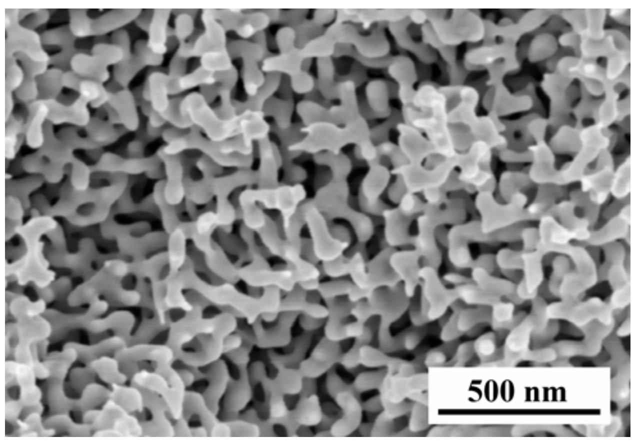
Figure caption:

Figure 1 SEM micrograph showing the characteristic sponge-like open-cell foam morphology of np-Au. The material is very homogeneous and exhibits nanometer-sized pores and ligaments, the latter with a length-to-diameter aspect ratio close to one.

Figure 2 Nanoindentation experiments on np-Au with a relative density of 0.25 as a function of ligament diameter. a, Series of load versus displacement (*P-h*) curves using a Berkovich tip. The shift of the *P-h* curves towards lower depths indicates that the indentation hardness and therefore the yield strength of np-Au increases with decreasing ligament diameter. **b,** SEM micrograph of the residual impressions of an array of indents, and a close-up of marked indent. Note that the plastic deformation is confined to the area under the indenter. **c,** Plot of yield strength of Au ligaments versus ligament diameter (open circles). Also shown is a data point obtained by a linear compression test using micron-sized columns of np-Au (filled circle) as well as a linear extrapolation of the yield strength data obtained from single crystal Au columns (solid line).[6]

Figure 3 Uniaxial micro-compression tests of np-Au. a, SEM micrograph of a 4 μm-diameter np-Au column with an aspect ratio of ~ 2:1 prepared by FIB micro-machining (after compression testing). Note that the characteristic pore structure of np-Au survives the FIB micro-machining. **b,** Stress-strain curve of a np-Au column. Note that despite this high porosity np-Au is as strong as bulk Au (30-200 MPa).



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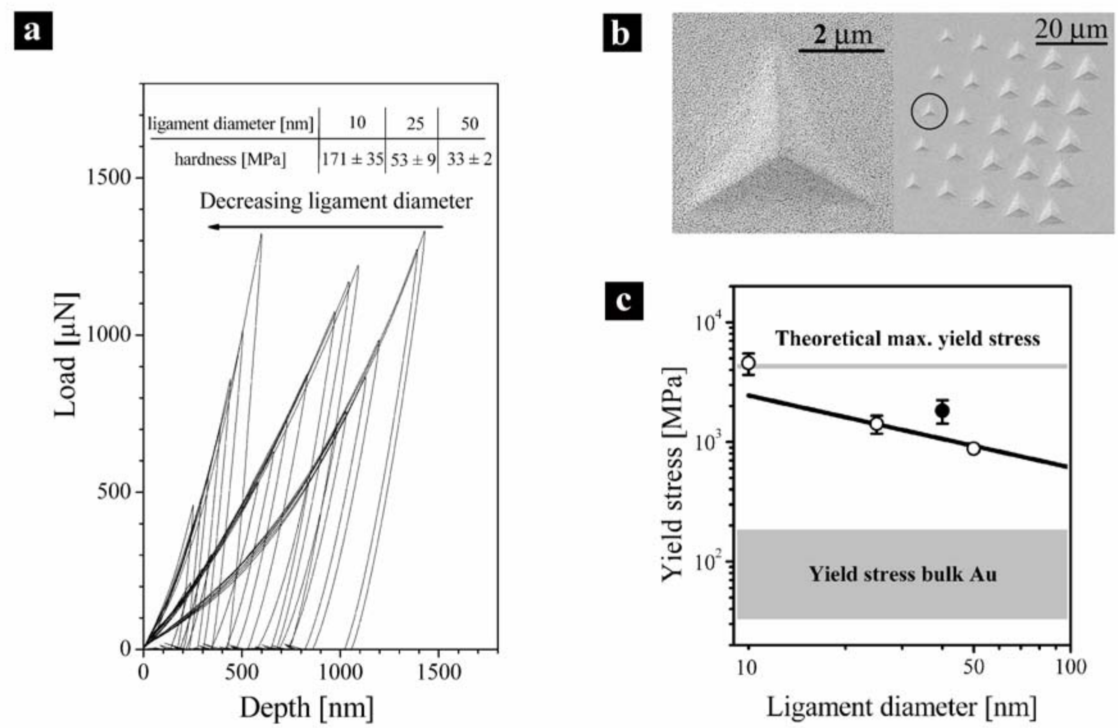

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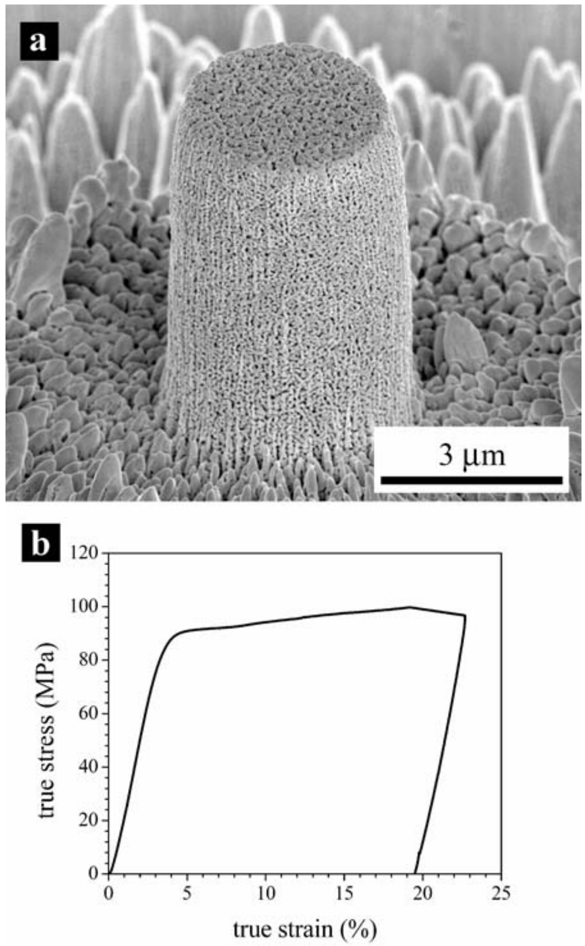

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